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Experimental Determination of Physical Properties of DNGU, TNBA, LLM-105, HK-56, and DNP

by Rose A Pesce-Rodriguez and Lauren B Blaudeau

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Experimental Determination of Physical Properties of DNGU, TNBA, LLM-105, HK-56, and DNP

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14. ABSTRACT

Chemical analysis of 5 energetic materials—1,4-dinitroglycloluril (DNGU or DINGU), 2,4,6-trinitro-3-bromoanisole (TNBA), diamino-3,5-dinitropyrazine-1-oxide (LLM-105 or ANPZO), 2,5,7-trinitro-2,5,7,9-tetraazabicyclo [4.3.0]nonane-8-one (HK-56), and 3,4-dinitropyrazole (DNP)—was performed. Results for the following are reported: octanol/water partition coefficient (K_{ow}); soil sorption constant (K_{oc}); water solubility; vapor pressure; heat of vaporization; Raman, Fourier transform IR, and UV spectra; differential scanning calorimetry; and thermogravimetric analysis traces. The hydrolysis half-life time for DNGU is also reported.

15. SUBJECT TERMS

solubility, K_{ow}, K_{oc}, octanol-water partition coefficient, soil sorption coefficient, hydroylysis, vapor pressure, heat of vaporization, DNGU, DINGU TNBA, LLM-105, HK-56, DNP, 1,4-dinitroglycloluril, diamino-3,5-dinitropyrazine-1-oxide, 2,4,6-trinitro-3-bromoanisole, 3,4-dinitropyrazole, 2,5,7-trinitro-2,5,7,9-tetraazabicyclo [4.3.0]nonane-8-one

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1. Background

The characterization results reported herein were obtained in support of Strategic Environmental Research and Development Program (SERDP) project WP-2208, "GrIMEx (Green IM Explosive): Development of Novel IM Comp B Replacements Based on Green TNT and RDX Replacements" led by Dr David Price, Holston Research and Development Manager, BAE Systems, Ordnance Solutions, Inc. (OSI), Holston Army Ammunition Plant (Kingsport, TN). The objective of the overall project is to "1) develop environmentally acceptable synthesis methods to scale-up environmentally sustainable, insensitive secondary explosives as alternatives to cyclotrimethylenetrinitramine (RDX), 2, 4, 6-trinitrotoluene (TNT), and ammonium perchlorate (AP); and 2) Develop novel formulations utilizing the alternative materials to replace Composition B (Comp B)" (Price et al. 2015).

The objective of this work reported is to determine the physical properties that are required for modeling of environmental fate and transport of 5 energetic materials: 1,4-dinitroglycloluril (DNGU), 2,4,6-trinitro-3-bromoanisole (TNBA) , diamino-3,5-dinitropyrazine-1-o×ide (LLM-105 or ANPZO), 2,5,7-trinitro-2,5,7,9-tetraazabicyclo [4.3.0]nonane-8-one (HK-56), and 3,4-dinitropyrazole (DNP).

2. Experimental

All samples were provided by Dr David Price (OSI, BAE Systems) and used without further purification. Structures, full names, abbreviations, molecular weight, and relative pH of all samples are given in Fig. 1.
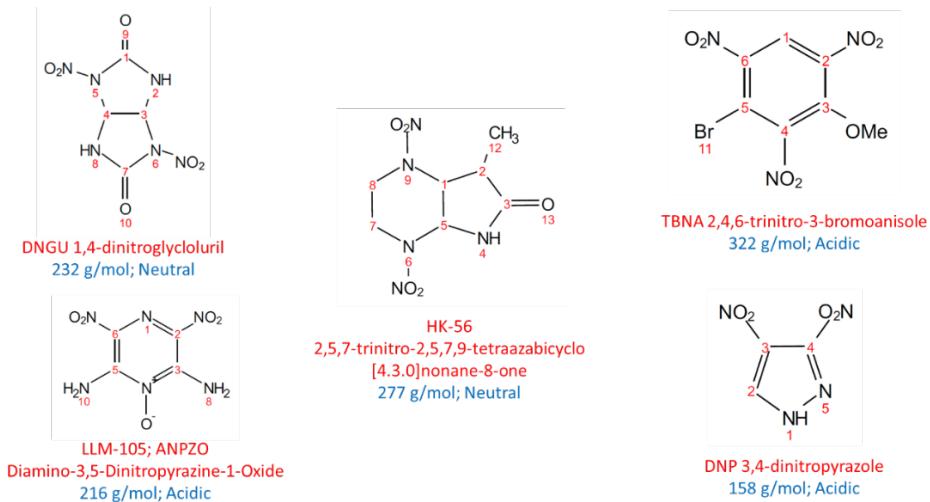
Fig. 1   Structures, names, abbreviations, molecular weight, and relative pH of samples in this study

Estimations of pH were obtained by placing solid material directly onto pH indicator strips (EMD Chemicals, Inc., Gibbstown, NJ) that had been pre-moistened with distilled, deionized water. Determination of pH was through visual comparison of the resulting strip color with a color chart provided by the manufacturer.

Differential scanning calorimetry (DSC) analyses were carried out using a TA Instruments (New Castle, DE) Q2000 instrument operating under TA Universal Analysis software. All samples were run in both standard pans and hermetic pans with pinhole lids at a heating rate of 10 °C/min under nitrogen (50 mL/min). Thermogravimetric analysis (TGA) was performed using a TA Q500 TGA. All analyses were run under an inert atmosphere (nitrogen flowing at 60 mL/min), in platinum pans, and at a heating rate of 10 °C/min from 25–450 °C.

Vapor pressure was estimated using the method given in Pesce-Rodriguez and Klier (2014). Heat of evaporation/sublimation was estimated by a Clausius-Clapeyron plot of estimated vapor pressures at 25, 70, and 100 °C.

Attenuated total reflectance (ATR)-Fourier transform infrared (FTIR) spectra were obtained using a Nicolet is50 spectrometer with an onboard ATR accessory. For each spectrum, 128 scans were collected at a resolution of 4 cm^{-1}. Raman spectra were obtained using a Nicolet is50 Raman system with a 1064-nm laser operating at a power of 50 mW. For each spectrum, 32 scans were collected at a resolution of 8 cm^{-1}. Spectral collection and analysis with these instruments was performed were obtained using Nicolet Omnic software.

Solubility determination was performed on saturated solutions of each material at ambient temperature (23 °C). Saturation was insured by adding material to high-performance liquid chromatography (HPLC) grade water and shaking for a minimum of 8 h. If solid material remained in the solution after that time, no further material was added. If all of the solid material had dissolved, more material was added and the solution was stirred for a minimum of an additional 8 h. The process was discontinued when solid material remained in the flask after an 8-h dissolution period. At this point, the solution was centrifuged (3000 rpm, 20 min at 23 °C) to separate any suspended solids. Supernatant solution was collected and analyzed by HPLC. Dilution was performed, if necessary, to prevent saturation of the detector. Quantitation was accomplished by means of a calibration curve constructed based on the HPLC peak areas of standard solutions prepared by adding preweighed, as-received material into known volumes of HPLC grade water.

The absorbance maximum for each compound was determined from a UV spectrum obtained on a USB4000 Ocean Optics UV/visible spectrometer. Concentration was determined in milligrams per milliliter. For HPLC analysis, an Agilent

Technologies 1200 Series HPLC with UV detection was used. The mobile phase consisted of 60% acetonitrile and 40% water at a constant flow rate of 1 mL/min. The column, an Agilent Technologies Pinnacle II C18 5-μm (250 × 4.6 mm) was maintained at a constant temperature of 23 °C. A sample injection volume of 10 μL was used. Because DNGU was found to rapidly hydrolyze, calibration standards were prepared in dimethyl sulfoxide (DMSO) and analyzed by liquid chromatography-mass spectrometry (LC-MS). For this analysis, an Agilent 1200 series HPLC with an Agilent single quadrapole MS detector was used. The HPLC mobile phase flow rate was reduced to 0.4 mL/min. For MS detection, the electron impact voltage was set to 70 eV. Quantitation was based on integration of the selected ion chromatogram for the parent ion (231; M-H) in the negative ion chromatogram.

K_{ow} determination was based on the Office of Prevention, Pesticides and Toxic Substances (OPPTS) 830.7550, *Partition Coefficient (n-Octanol/Water), Shake Flask Method* (1996). Analytical grade octanol and water were mutually presaturated by stirring at 23 °C. The solvents were then allowed to stand to permit phase separation and achieve a saturated state. For each sample (prepared in duplicate) the minimum amount of analyte was added to 2 mL of water (presaturated with octanol) and 1, 2, or 4 mL of octanol (presaturated with water). (Determination of the minimum amount of sample necessary was based on the guidance in OPPTS 830.7550 that the maximum concentration in either phase could not exceed 0.01-mol/L.) For the larger samples containing 4 mL of octanol, preparation was in 20-mL glass vials; otherwise, 4-mL glass vials were used. All phases of the analysis were conducted at 23 °C. The test vessels were manually shaken by quickly rotating the vials through 180° about their transverse axis so that trapped air rose through the 2 phases. No less than 100 rotations in 5 min were performed, as per the guidance in OPPTS 830.7550. All vials were subsequently centrifuged at 3000 rpm for 10 min at 23 °C. After centrifugation, the phases were separated and analyzed by HPLC as described earlier for solubility samples. K_{ow} was determined using Eq. 1:

$$K_{ow} = \frac{\text{Concentration of analyte in n−octanol (presaturated with water)}}{\text{Concentration of analyte in water (presaturated with n−octanol)}} . \tag{1}$$

Determination of K_{oc} was performed in accordance with American Society for Testing and Materials (ASTM) E1195-01, *Standard Test Method for Determining a Sorption Constant (K_{oc}) for an Organic Chemical in Soil and Sediments* (2001). Soil-to-sample ratios were selected to achieve between 20% and 80% sorption. Analyses were conducted in 4-mL glass vials containing 2 mL of sample solution and 1 g of Sassafras sandy loam (SSL) soil. Results of the physical and chemical characterization of the SSL soil material are given in Table 1. As per ASTM E1195-

01, the initial analyte concentration in should not exceed 0.5 times the given compound's water solubility. For this analysis, the initial concentration was reduced to not more than 0.1 times the water solubility in an attempt to increase the percentage of material sorbed. Control samples consisted of an aqueous solution of analyte with no soil and distilled water (no analyte) with soil. All samples were prepared in duplicate. Samples were agitated on a wrist-action shaker for a minimum time of 48 h, and then centrifuged (3000 rpm, 20 min at 23 °C) before being analyzed by HPLC using the same conditions used for solubility determination.

Table 1   Information on SSL. (SSL provided by Dr Michael Simini, Edgewood Chemical Biological Center.)

Soil Testing Results
Sassafras Soil Characterization — SSL2007d
Sieved 5mm; air dried — Collected from M-Field 6/21/2007

FIELD ID	pH	OM	Sand	Silt	Clay	CEC	Conductivity	Mg	Soil Type	Texture
		%	%	%	%	cmol/kg	mmhos/cm	mg/kg		
SSL20070702-1	4.9	2.3	53.7	28.1	18.2	8.8	ND	84	Sassafras	sandy loam
SSL20070702-2	4.9	2.2	55.3	26.0	18.7	10.2	ND	90	Sassafras	sandy loam
SSL20070702-3	4.9	2.3	55.8	29.9	16.5	8.9	ND	87	Sassafras	sandy loam
MEAN	4.9	2.3	54.9	28.0	17.8	9.3		87.0		
STD ERR	0.00	0.03	0.63	1.13	0.67	0.45		1.73		

	P	K	Ca	N (NO3)	N (NH4)	Mn	Zn	Cu	Fe
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
SSL20070702-1	7	68	324	ND	ND	ND	10.7	7.6	ND
SSL20070702-2	6	78	347	ND	ND	ND	11.1	9.1	ND
SSL20070702-3	6	76	335	ND	ND	ND	12.2	9.0	ND
									ND
MEAN	6.3	74.0	335.3				11.3	8.6	
STD ERR	0.33	3.06	6.64				0.45	0.48	

Sassafras sandy loam (SSL), a fine-loamy, siliceous, semiactive, mesic Typic Hapludult collected from an open grassland field in the coastal plain on the property of the U.S. Army Aberdeen Proving Ground, Harford County, MD

Soil was analyzed for physical and chemical characteristics by Cooperative Extension Service, University of Maryland Soil Testing Laboratory, College Park, MD

ND = Not Determined

Note: OM = organic matter

Prior to deciding on which solids (soil)-to-water ratio to use for K_{oc} determination, it is advised in ASTM E1195-01 to first estimate K_{oc} using the Eq. 2, which predicts K_{oc} values within an order of magnitude.

$$ln\ K_{oc} = (-ln\ Ws - 0.01\ (MP\text{-}25) + 15.1621)/1.7288, \qquad (2)$$

where Ws = water solubility (mg/L), and MP = melting point (°C; from DSC analysis). (Use the decomposition temperature if the sample does not melt.)

K_d, the sorption coefficient, factors in the organic matter (OM) content of the soil sample and is estimated from Eq. 3:

$$K_d = (K_{oc}) \ (\% \ \text{organic carbon}/100). \tag{3}$$

Experimental K_d and K_{OC} values are calculated using Eqs. 4 and 5.

$$K_d = \frac{\mu g s \ \text{chemical/g solids}}{\mu g w \ \text{chemical/g } H2O}, \tag{4}$$

where K_d = sorption coefficient, $\mu g s$ = chemical sorbed, μg, and $\mu g w$ = chemical in solution at equilibrium, μg, and

$$K_{oc} = \frac{K_d \times 100}{\% \ OC}, \tag{5}$$

where K_{oc} = organic carbon normalized sorption constant, K_d = sorption distribution coefficient, and % OC = percentage of organic carbon in solids.

3. Results and Discussion

UV spectra used to determine λ_{max} for HPLC analysis are given in Fig. 2. Raman and FTIR spectra are given in Figs. 3 and 4, respectively. The spectra show no indication of unexpected impurities. Results from DSC analysis are given in Figs. 5–9. Melting or decomposition temperatures needed for K_{oc} prediction were obtained from these DSC traces. Differences in the traces for standard pans (unsealed) and hermetic pans with pinhole lids are ascribed to loss of sample from the standard pans as a result of evaporation or sublimation. This is especially obvious for TNBA (Fig. 6), which shows no decomposition exotherm when an unsealed standard pan is used.
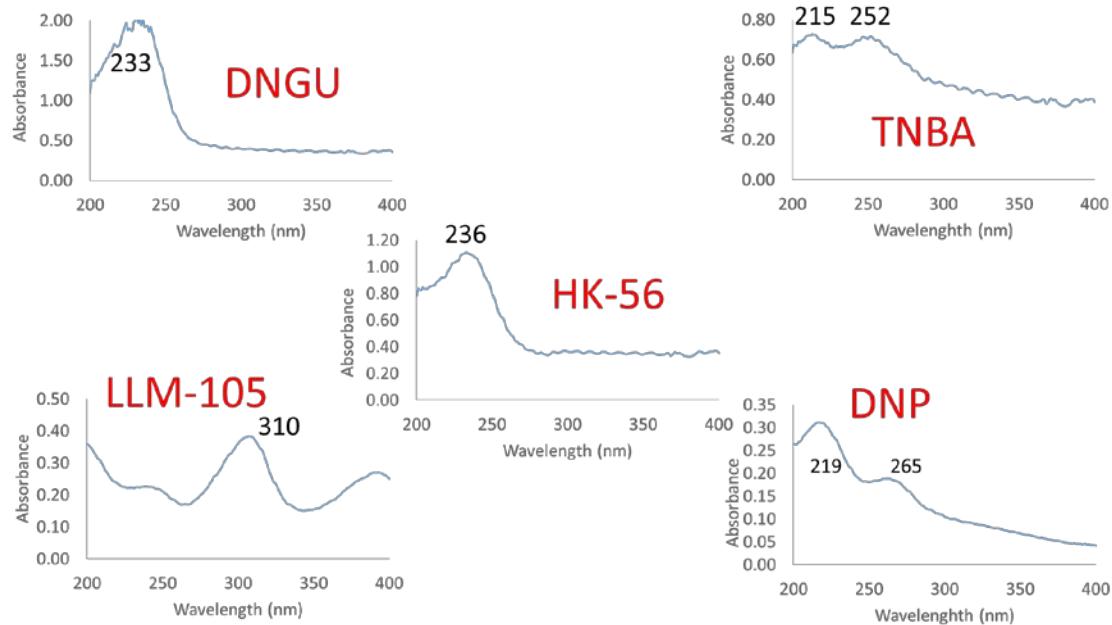
Fig. 2   UV spectra of samples in this study. Absorbance wavelength maxima are indicated for each spectrum.
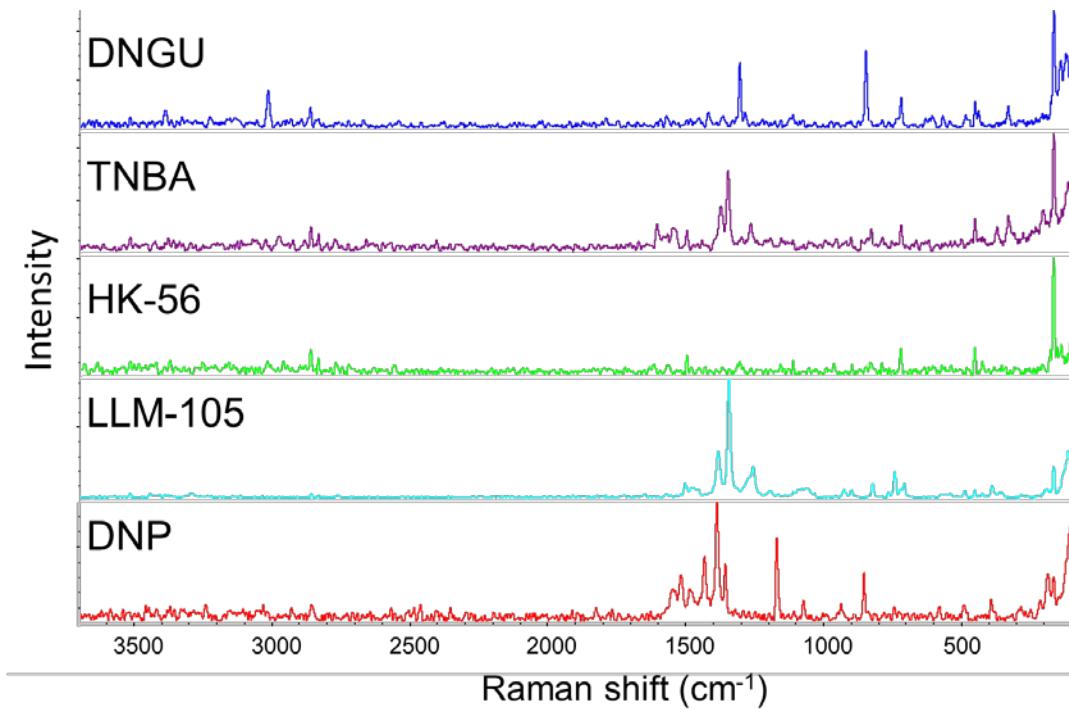
Fig. 3   Raman spectra of samples in this study

6
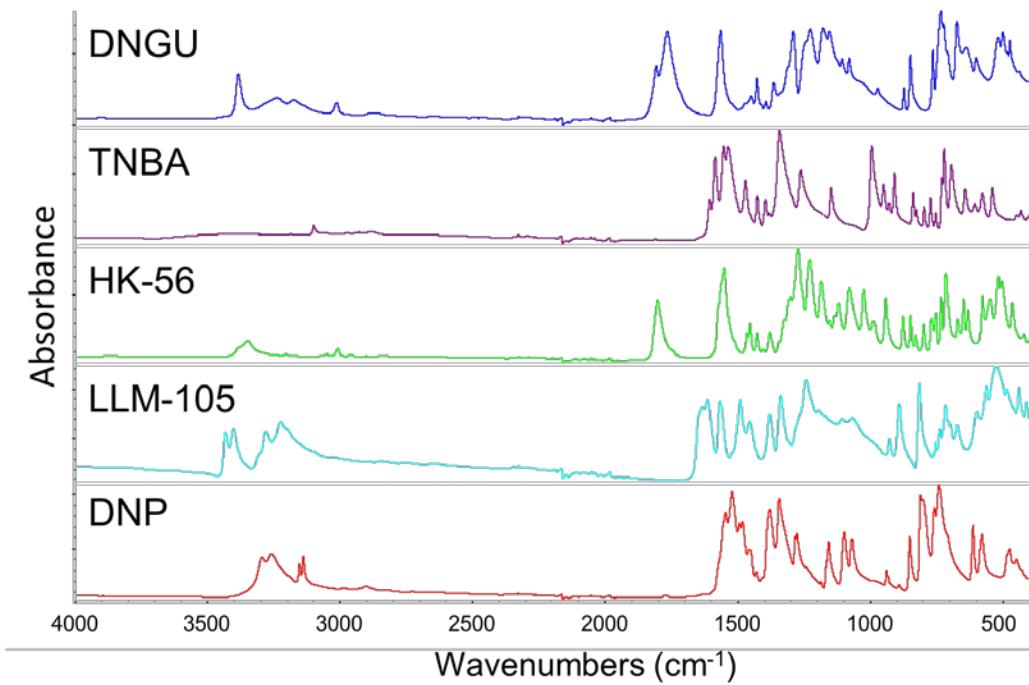
Fig. 4   ATR-FTIR spectra of samples in this study
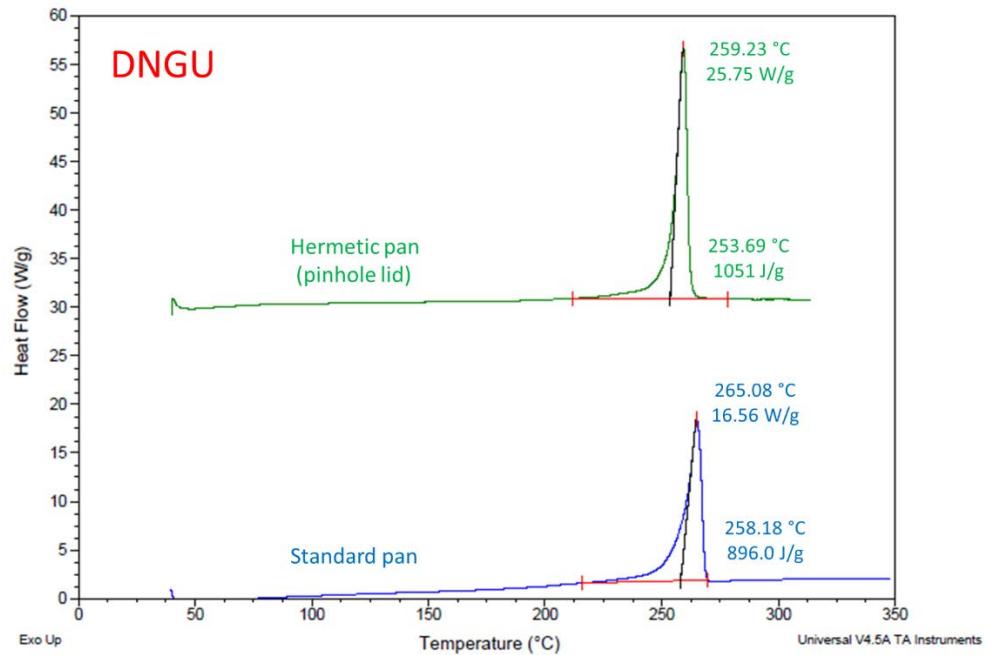
Fig. 5   DSC trace for DNGU. Heating rate: 10 °C/min under nitrogen. Top trace (blue): hermetic pan with pinhole and bottom trace (green): standard pan.
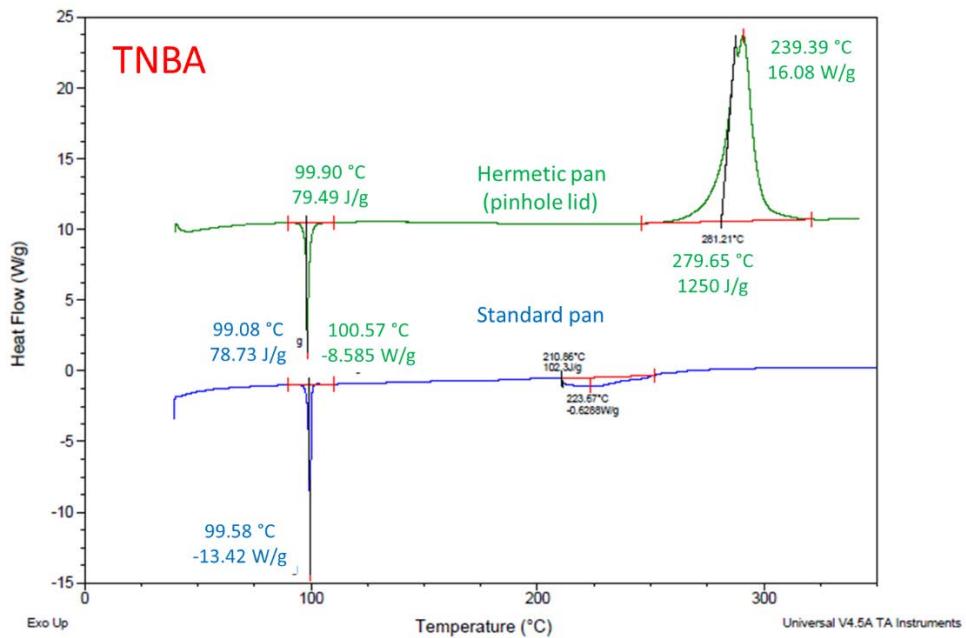
Fig. 6   DSC trace for TNBA. Heating rate: 10 °C/min under nitrogen. Top trace (blue): hermetic pan with pinhole and bottom trace (green): standard pan. The vapor pressure of TNBA is sufficiently high that the sample in the standard pan completely volatilizes before decomposition. Decomposition exotherm is observed when the sample is analyzed in a hermetic pan (with pinhole lid), which suppresses volatilization.
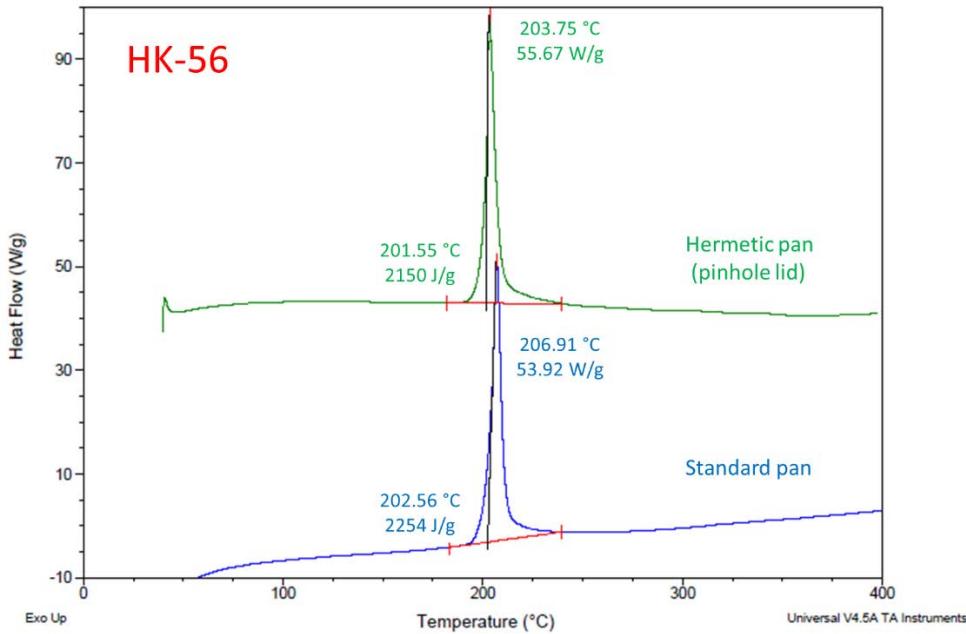
Fig. 7   DSC trace for HK-56. Heating rate: 10 °C/min under nitrogen. Top trace (blue): hermetic pan with pinhole and bottom trace (green): standard pan.
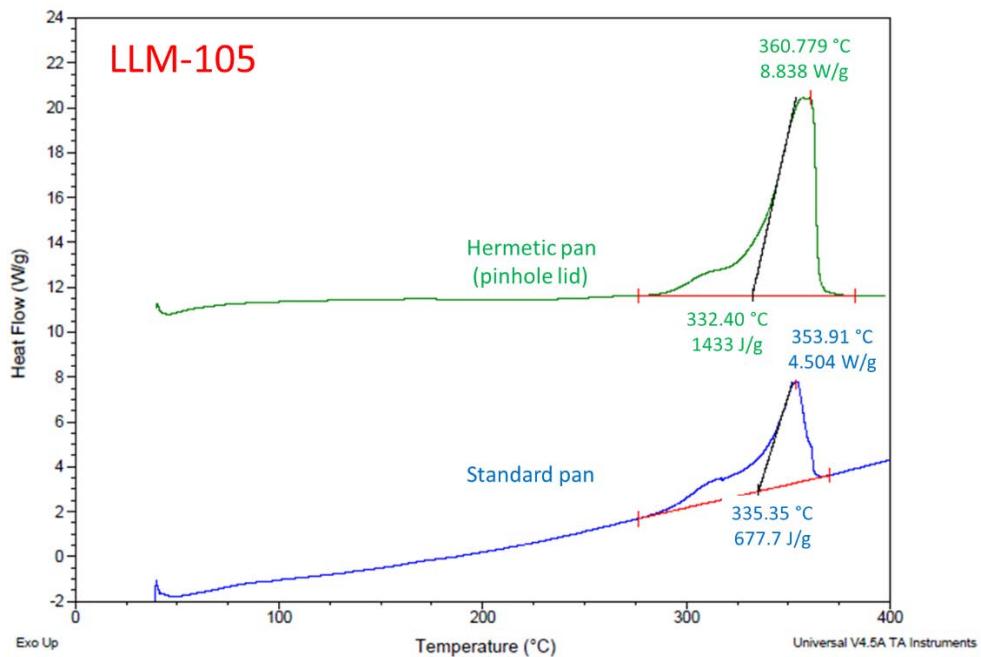
Fig. 8 DSC trace for LLM-105. Heating rate: 10 °C/min under nitrogen. Top trace (blue): hermetic pan with pinhole and bottom trace (green): standard pan.
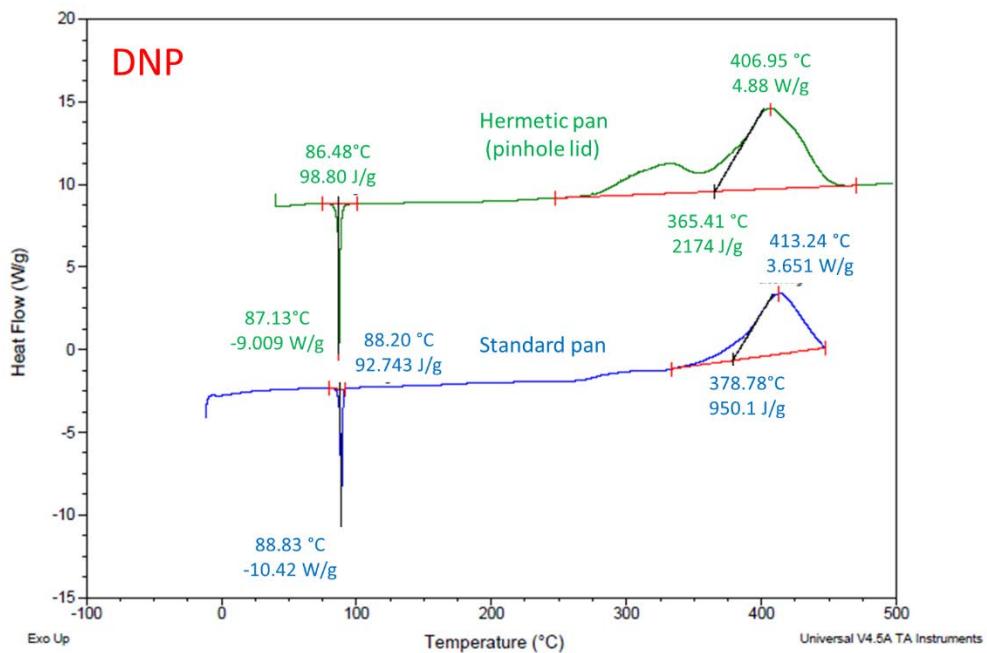
Fig. 9 DSC trace for DNP. Heating rate: 10 °C/min under nitrogen. Top trace (blue): hermetic pan with pinhole and bottom trace (green): standard pan.

TGA traces are given in Fig. 10, and were used to predict vapor pressure and heat of vaporization. A summary of these values are given in Table 2. Values for TNT, RDX, and HMX are also given for reference. Unfortunately, there is very little information in the literature that can be used to compare with the estimated values. ChemSpider (2015) reports calculated values of 0.3 Torr and 129.6 kJ/mol for the vapor pressure at 25 °C and heat of vaporization for LLM-105. The estimated vapor pressure from this work is substantially lower than the ChemSpider value, while the heat of vaporization agrees reasonably well. The range of estimated heats of vaporization for the 5 compounds of interest are all well above those for TNT. Only TNBA has a lower heat of vaporization than RDX. Considering this, it is not surprising that all 5 compounds also have vapor pressures below that of TNT and that only TNBA has a vapor pressure higher than that of RDX.
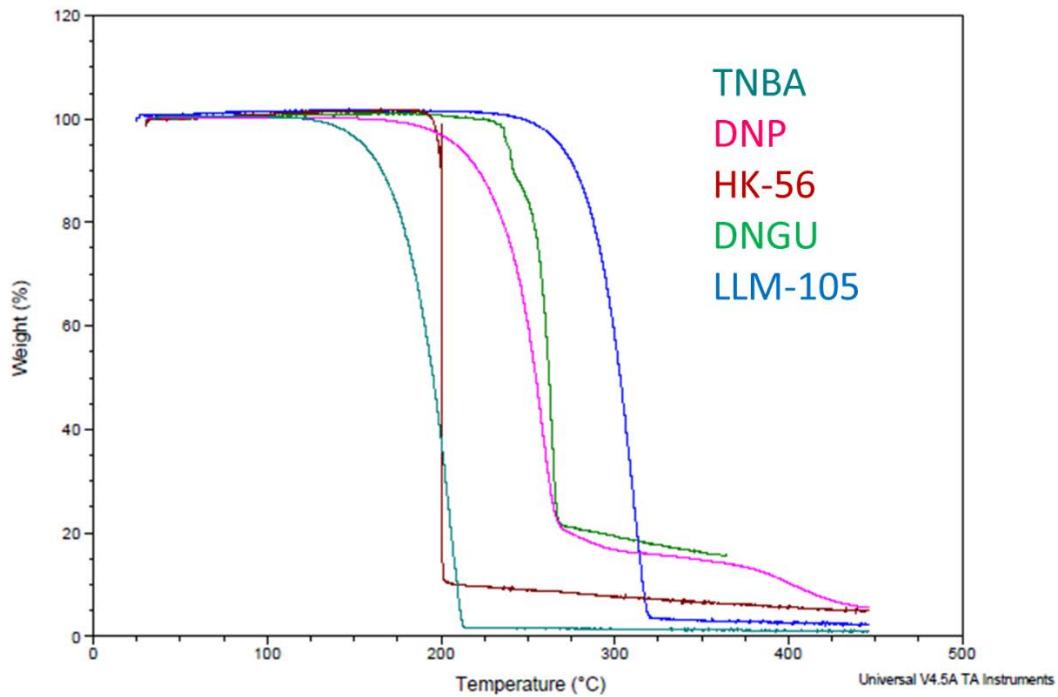
Fig. 10   TGA traces for all samples in this study. Heating rate: 10 °C/min under nitrogen.

Table 2   Summary of estimated vapor pressures and heats of vaporization (ΔH_{vap}). Compounds in red decompose without melting. Compounds in green melt before decomposition. Estimations made using method reported in Pesce-Rodriguez and Klier (2014).

Sample	VP (Torr; estimated)			ΔH_{vap} (estimated) (kJ/mol)
	25 °C	70 °C	100 °C	
LLM-105	$8.50 \ 10^{-16}$	9.15×10^{-13}	50.4×10^{-10}	163.8
DNGU	2.54×10^{-13}	2.06×10^{-10}	5.40×10^{-08}	151.2
HK-56	1.52×10^{-12}	1.13×10^{-09}	2.35×10^{-07}	147.3
DNP	2.42×10^{-11}	1.57×10^{-08}	2.72×10^{-06}	141.4
TNBA	1.59×10^{-07}	6.66×10^{-05}	3.08×10^{-03}	121.7
TNT*	5.50×10^{-06}	2.31×10^{-03}	5.77×10^{-02}	114.1
RD×*	3.30×10^{-09}	2.76×10^{-06}	9.92×10^{-05}	127.1
HM×*	3.01×10^{-15}	3.14×10^{-11}	4.37×10^{-09}	174.7

* Experimental values cited in Ostmark et al. (2012).

Results for experimentally measured water solubilities (at 23 °C), octanol-water partition coefficients, and soil sorption coefficients are given in Table 3. A summary of predicted and measured K_{oc} values is given in Table 4 and shows that as per the general guidance in ASTM E1195-01, the predicted and measured values for each compound differ by no more than an order of magnitude. In most cases, the values differ by a factor of just 2–3. No value for the K_{oc} of DNGU is reported because it was found to have a hydrolysis half-life time of approximately 90 min (Fig. 11). Meyer et al. (2016) note that DNGU is stable in neutral water, but it appears that DNGU, like tetranitroglycolurile is subject to hydrolysis in neutral solution (Sherrill and Johnson 2014; Chapman et al. 2009).

From a green propellant point of view, this property is a great advantage because the material will have no tendency to persist in either soil or water. Because the ASTM method for K_{oc} determination calls for shaking an aqueous solution of analyte with the soil for 48 h, determination of K_{oc} was not possible, and we have only the predicted value listed in Table 4 (K_{oc} = 1482) to report. Reasonable estimations of water solubility and K_{ow} were obtained by preparing DNGU standards in DMSO and analyzing by LC-MS. UV detection of the DNGU standards could not be performed because of the spectral overlap of DMSO and DNGU. Solubility measurement was accomplished by analysis of a saturated solution. It was assumed that DNGU hydrolysis products present in the solution would not interfere with the quantitative analysis. Because K_{ow} sample preparation requires only 5 min of shaking, a quick analysis of the aqueous phase following shaking allowed for a good approximation of K_{ow} for DNGU.

Table 3   Summary of solubility, K_{ow} and K_{oc} results for the compounds studied

Sample	Solubility (mg/mL)	K_{ow}	Log K_{ow}	K_d	K_{oc}	log K_{oc}
DNGU	1.4×10^{-01}	0.253	−0.60	…	…	…
TNBA	8.7×10^{-03}	0.017	−1.8	19.4	843	2.92
LLM-105	1.4×10^{-02}	0.058	−1.2	2.86	124	2.09
HK-56	5.1×10^{-01}	0.016	−1.8	0.92	40.3	1.61
DNP	6.7×10^{-01}	4.7	0.67	0.673	29.3	1.47
TNT*	1.5×10^{-01}	100	2.0	12.1	524	2.72
RDX*	6.0×10^{-02}	7.41	0.87	2.3	100	2.0
HMX*	5.0×10^{-03}	1.82	0.26	0.080	3.46	0.54

* Burrows et al. (1989).

Table 4   Summary of predicted and measured K_{oc} results for the compounds studied

Sample	Predicted K_{oc}	Measured K_{oc}
DNGU	1482	----
TNBA	1203	843
LLM-105	209	124
HK-56	61.5	40.3
DNP	7.23	29.3
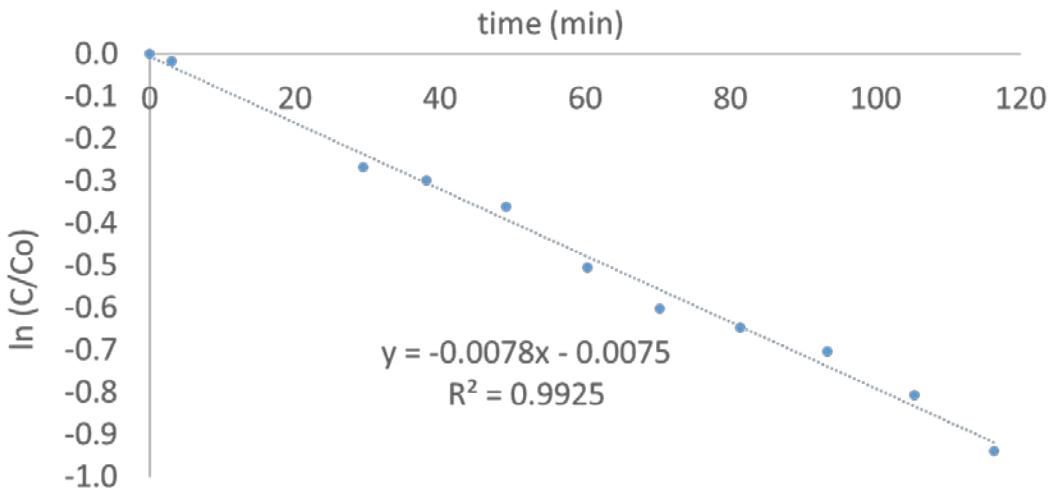
Fig. 11   Results of the DNGU hydrolysis study. Hydrolysis half-life was determined to be approximately 90 min.

ChemSpider (2015) offers a calculated log K_{ow} for LLM-105 of 3.84 and a K_{oc} of 78.28. While our measured value for K_{oc} (124) compares favorably, the log K_{ow} (−1.2) does not.

Boddu et al. (2010) report theoretical values of solubility and K_{ow} for DNP. Their value for solubility (733 mg/L) is an order of magnitude larger than our experimental determination (67 mg/mL). Boddu et al. report a K_{ow} value of 0.37

and note other theoretical values by Broto et al. (1984), 0.9, and Ghose et al. (1988), –0.99. While Boddu et al.'s table refers to K_{ow}, not log K_{ow}, the negative sign in the Ghose et al. value indicates that it must be log K_{ow} to which they are referring. Our measured value (0.67) falls between the Broto et al. and Boddu et al. calculated values. The positive sign suggests that DNP has an affinity for OM, which was quite surprising given its relatively high water solubility. DNP was the only compound in the sample set that "oiled out" when its saturation limit was exceeded. Of course, "oiling out" has nothing to do with a material being oil-like, but is instead a phenomenon related to crystallization and phase separation. Determination of both K_{ow} and K_{oc} are carried out at sufficiently low concentrations that oiling out is not expected to be a problem.

No theoretical or experimental results for any of the other values reported herein could be found in the literature.

4. Conclusions

A set of 5 energetic materials being considered as RDX and TNT replacements for green insensitive munitions applications were analyzed with the objective of determining physical properties required for environmental fate and transport modeling.

All 5 test samples were observed to have lower vapor pressures than TNT, and only TNBA was observed to have a vapor pressure higher than RDX.

DNP was found to be fairly soluble in water (100 times as soluble as TNT and 1,000 times as soluble as RDX). It was also found to be at least partially soluble in octanol, as indicated by its positive log K_{ow} value. DNP, as well as the other 4 test samples, did, however, have a lower K_{ow} value than RDX and a far lower K_{ow} than TNT, suggesting that they will have low soil/sediment adsorption coefficients and also have less of a tendency to bioconcentrate in aquatic life. The former is confirmed by the experimentally determined soil sorption coefficient for LLM-105, HK-56, and DNP, which are all considered to have low (1–100) K_{oc} values, and TNBA, which has a moderate (100–100,000) K_{oc} value. Only TNBA has a higher K_{oc} than that of RDX and TNT.

For all compounds but one, experimental values for solubility, K_{ow} and K_{oc} were successfully determined. Because DNGU was observed to hydrolyze in neutral water, measurements of only solubility and K_{ow} were possible. The hydrolysis half-lifetime in neutral water was found to be approximately 90 min. Estimates of vapor pressures at 25, 70, and 100 °C and heats of vaporization were also determined for each of the 5 energetic samples. Comparisons with the few theoretical values for

solubility and K_{ow} in the literature suggest that the measured values reported herein are reasonable and appropriate for use in fate and transport models.

Of all 5 test samples, DNGU is expected to be the least persistent in the environment. It has a relatively low vapor pressure and readily hydrolyzes in neutral water. Characterization of hydrolysis products was not performed, but should be done to confirm that they do not pose their own an environmental or toxicological hazards. From a service life perspective, the tendency of DNGU to hydrolyze may pose a problem and should be considered before moving forward with formulation.

LLM-105 and HK-56 also have low vapor pressures and relatively low water solubilities, K_{ow} and K_{oc}. Neither appears to hydrolyze in neutral water. Hydrolysis studies in acidic/basic water were not performed, nor were photolysis studies. These could be done in the future if deemed necessary by the SERDP program.

TNBA has a relatively high vapor pressure (higher than RDX, but lower than TNT). It also has a relatively low water solubility (just slightly higher than HMX), a low K_{ow}, and a moderate K_{oc}. As noted for LLM-105 and HK-56, photolysis and acid/base hydrolysis behavior were not investigated but could be done, if necessary.

DNP is expected to be fairly mobile and persistent in ground water as it has a relatively high solubility and does not hydrolyze in neutral water (hydrolysis behavior in acid/base was not examined). DNP's low vapor pressure suggests that it does not readily volatilize, and its low K_{ow} and K_{oc} values suggest that it will not tend to adsorb on OM or bioconcentrate.

5. References

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List of Symbols, Abbreviations, and Acronyms

AP	ammonium perchlorate
ASTM	American Society for Testing and Materials
ATR	attenuated total reflectance
DMSO	dimethyl sulfoxide
DNGU	1,4-dinitroglycloluril
DNP	3,4-dinitropyrazole
DSC	differential scanning calorimetry
FTIR	Fourier transform infrared
HK-56	2,5,7-trinitro-2,5,7,9-tetraazabicyclo
HPLC	high-performance liquid chromatography
IR	infrared
LC	liquid chromatography
LLM-15 or ANPZO	diamino-3,5-dinitropyrazine-1-o×ide
MS	mass spectrometry
OM	organic matter
OPPTS	Office of Prevention, Pesticides and To×ic Substances
OSI	Ordnance Solutions, Inc.
RDX	cyclotrimethylenetrinitramine
SERDP	Strategic Environmental Research and Development Program
SSL	Sassafras sandy loam
TGA	thermogravimetric analysis
TNBA	2,4,6-trinitro-3-bromoanisole
TNT	2, 4, 6-trinitrotoluene
UV	ultraviolet

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